

DEPARTMENT OF COMMERCE

SCIENTIFIC PAPERS
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BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 335

EFFECT OF RATE OF TEMPERATURE CHANGE
ON THE TRANSFORMATIONS IN AN
ALLOY STEEL

BY

HOWARD SCOTT, Assistant Physicist
Bureau of Standards

ISSUED JULY 10, 1919



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THE TRANSFORMATIONS IN AN ALLOY STEEL

By Howard Scott

CONTENTS

	Page
I. Introduction.....	91
II. Previous investigations.....	92
III. Experimental method.....	93
IV. Thermal curves.....	93
V. Effect of cooling rate.....	96
1. Microstructure.....	96
2. Relation of Ar' to Ar''.....	97
3. Suppression of Ar'.....	97
VI. Transformations on heating.....	98
1. Transformation AcI.....	98
2. Effect of previous cooling rate on AcI-3.....	99
VII. Summary.....	100

I. INTRODUCTION

Since Böhler discovered in 1903, on cooling certain alloy steels, the phenomenon of a new and lower temperature transformation than the usual Ar_{3-2-1} obtained by increasing the maximum temperature (T_{max}) to which the material was heated, a considerable amount of work has been published,¹ connecting this phenomenon with a large number of dissimilar steels of high alloy content. From the fact that the transformation divides itself, taking place at two widely separated temperatures, it has been called a split transformation. The significant facts established by recent investigators ² are (a) that when the transformation occurs at the higher temperature, Ar' , troostite or a decomposition product is formed and (b) that when the transformation occurs at the lower temperature, Ar'' , the resulting structure is martensite. The terminology Ar' and Ar'' , adopted here, is that of Portevin.³

¹ Yatsevitch, Rev. de Met., 15, p. 65; 1918, Bibliography to 1915.
² Dejean, Rev. de Met., 14, p. 641; 1917. Portevin, ibid., 14, p. 707; 1917. Edwards, J. Iron and Steel Inst., 93, p. 114; 1916.
³ Portevin, loc. cit.

II. PREVIOUS INVESTIGATIONS

Reviewing the work on this subject ⁴ published in a recent issue of *Revue de Metallurgie* and referring in particular to his statement that martensite is a solution of carbide in alpha iron, H. Le Chatelier says:

How then can a theory already 20 years old demand new investigations? The reason for it is that we have not succeeded in proving directly the real presence of the transformation of iron during the very short duration of the quenching. The fall of temperature takes place at the rate of several hundred degrees per second and the observation of phenomena so rapid requires particularly sensitive methods of recording. I have attempted without success to observe the moment of the reappearance of the magnetic property during the quenching of bars 15 mm square, but the inequalities of temperature from one point to another in the mass conceal the phenomenon. M. Chevenard ⁵, in working on wires of a diameter 100 times smaller and using as a characteristic of the transformation of iron the change of length instead of the variation of magnetism, has surmounted for the first time the difficulties which seemed at first view insurmountable, and he has done it with an extreme precision. The thermal measurements of Portevin and Garvin ⁶ and of Dejean ⁷ lead to the same conclusions, although in a fashion less direct.

The results presented here add further confirmation of the theory of Le Chatelier, though in a less direct manner than those of Chevenard. Thermal and microscopic data are brought forward here to establish the effect of rate of temperature change on the temperature and nature of the transformations in a steel of the composition C, 1.75; Mn, 0.26; Co, 2.90; Cr, 15.0.

Similar work has been done by Edwards ⁸ on a steel of the composition C, 0.63; Cr, 6.15; Si, 0.07; Mn, 0.17.

However, he arrives at the conclusion that—

The maximum hardness was obtained when the thermal transformation had been entirely prevented, and when this was accomplished the steel was purely martensitic in structure.

The present work fails to confirm this statement, as does that of the investigators already referred to. Edwards was unable to observe the transformation Ar'' with the formation of martensite, probably for the reasons given by Rosenhain ⁹ in his discussion of Edwards' paper.

Yatsevitch, ¹⁰ Dejean ¹¹, and Honda ¹² have used two or three cooling rates in their experiments with varying $T_{max.}$, and their results show, as do Edwards's that the transformation split occurs for lower values of $T_{max.}$ with faster cooling rates.

⁴ Le Chatelier, *Rev. de Met.*, **14**, p. 601; 1917.

⁵ Chevenard, *Rev. de Met.*, **14**, p. 610; 1917.

⁶ Portevin and Garvin, *Rev. de Met.*, **14**, p. 607; 1917.

⁷ Dejean, *Rev. de Met.*, **14**, p. 641; 1917.

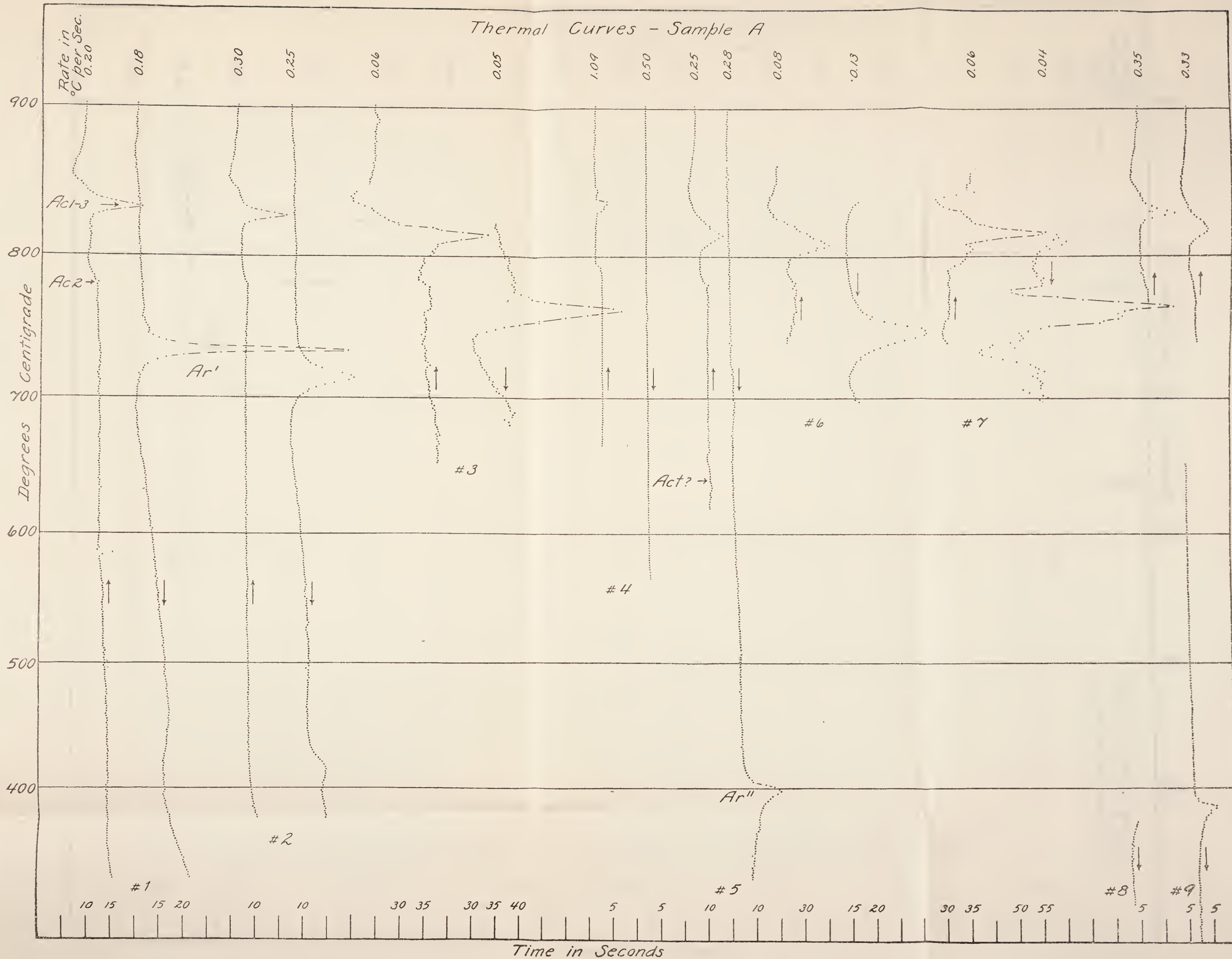
⁸ Edwards, *loc. cit.*

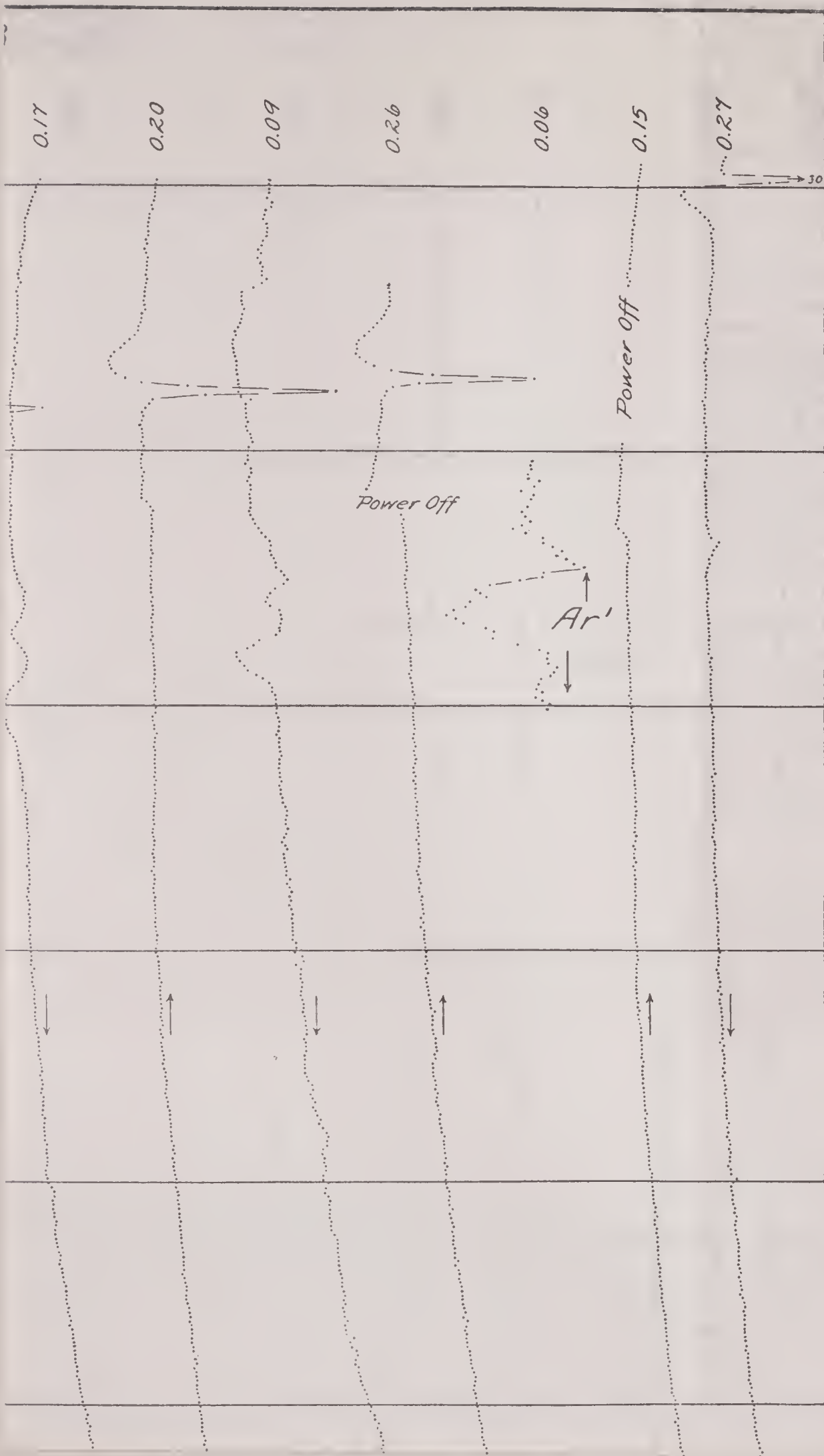
⁹ Rosenhain, *J. Iron and Steel Inst.*, **93**, p. 147; 1916.

¹⁰ Yatsevitch, *loc. cit.*

¹¹ Dejean, *loc. cit.*

¹² Honda and Murakami, *Sci. Rep. Tohoku Imp. Univ.*, **6**, p. 235; 1918.





The previous investigators in this field have laid particular stress on the variation of $T_{\max.}$, the rate remaining constant, while the variation of rate, $T_{\max.}$ remaining constant, has received little attention. The present work attempts to apply the latter method to the investigation of an alloy steel with the object in view of correlating the results of that method with those of the former and to establish the relationship between the several phenomena observed.

III. EXPERIMENTAL METHOD

The method employed for obtaining the thermal curves was to heat the samples, attached to the hot junction of a 0.5 mm diameter platinum, 90 platinum-10 rhodium thermocouple, in an electric vacuum furnace, taking potential measurements on a dial potentiometer and measuring the time interval on a chronograph, as described in the Bureau of Standards Scientific Paper 213. The furnace, however, was one recently built at the Bureau, a modified form of the one described by Rosenhain¹³ and in use at the National Physical Laboratory. This furnace, which will be described at a later date, was admirable for the purpose at hand, as extreme rates of temperature change can be obtained with smooth curves over long ranges.

IV. THERMAL CURVES

The curves of Figs. 1 and 2 were plotted by the inverse rate method from readings taken every 0.02 millivolt (approximately 2°C) except for several extremely fast runs, which, however, are plotted on that basis.

The curves of Fig. 1 are a preliminary series taken on sample A of about 10 g mass to locate the transformation ranges and without fully knowing the characteristics of the material. The data for the curves of Fig. 2 were taken on sample B, mass 0.81 g, keeping $T_{\max.}$ constant and extending the observations to lower temperatures than for sample A. The values given for rate of temperature change were reduced from the inverse rate curve observations taken on heating just before $Ac1-3$ and on cooling midway between Ar' and Ar'' .

The transformations as designated on the curves of Figs. 1 and 2 are Act , an evolution of heat on heating a sample previously cooled at a rate that gave Ar'' ; $Ac2$, the magnetic transformation; $Ac1-3$, the transformations $Ac1$ and $Ac3$ merged or nearly superimposed; Ar' , the upper transformation of the split Ar transformations; and Ar'' , the lower transformation. The temperature values of these transformations are collected in Table 1.

¹³ Rosenhain, *Inst. of Metals*, 13, p. 164; 1915.

TABLE 1.—Temperature Ranges of Transformations in Degrees Centigrade

SAMPLE A

Run	Rate of heating °C. per second	Acl			Ac2	Acr-3			Rate of cooling °C. per second	Ar'			Ar''			T max.
		Begin-ning	Maxi-mum	End		Begin-ning	Maxi-mum	End		Begin-ning	Maxi-mum	End	Begin-ning	Maxi-mum	End	
First.....	0.20				781	825	834	856	0.18	757	735					1050
Second.....	.30				781	819	829	855	.25	742	715	691	446	414	395	1125
Third.....	.06				780		816	841	.05		760	740				1110
Fourth.....	1.09				782		836		.50							970
Fifth.....	.25				781	804	816	847	.28	755		670	422	396	357	925
Sixth.....	.08				780	794	809	836	.13	772	748	714				880
Seventh.....	.06					809	817	841	.04	776	766	734				870
Eighth.....	.35				778	821	831	854	.80							925
Ninth.....	.33					809	819	847	.71				401	385	318	925

SAMPLE B

First.....										(^a)							920
Second.....	0.27	592	637	644	780	808	818	840	1.20				381	373	340		920
Third.....	.31	578	634	644	780	809	816	832	.60	748?	706	681	429	{409} {394}	371		920
Fourth.....	.31	544	601	628	779	808	816	832	.50	740	711	681	442	{423} {405}	387		920
Fifth.....	.33	518	621?	637	778	813	818	835	.43	748	{719} {694}	680	449	{430} {410}	392		920
Sixth.....	.20	564	601?	628	778	807	818	829	.17	759	{743} {719}	700					920
Seventh.....	.20				778	814	824	835	.09	775	{751} {736}	723					920
Eighth.....	.26					821	829	842	.06	770	756	738					920

^a Rate of cooling too fast for close observations.

The appropriateness of the transformation notation $Ac1-3$ and Act will be seen from the discussion of those transformations.

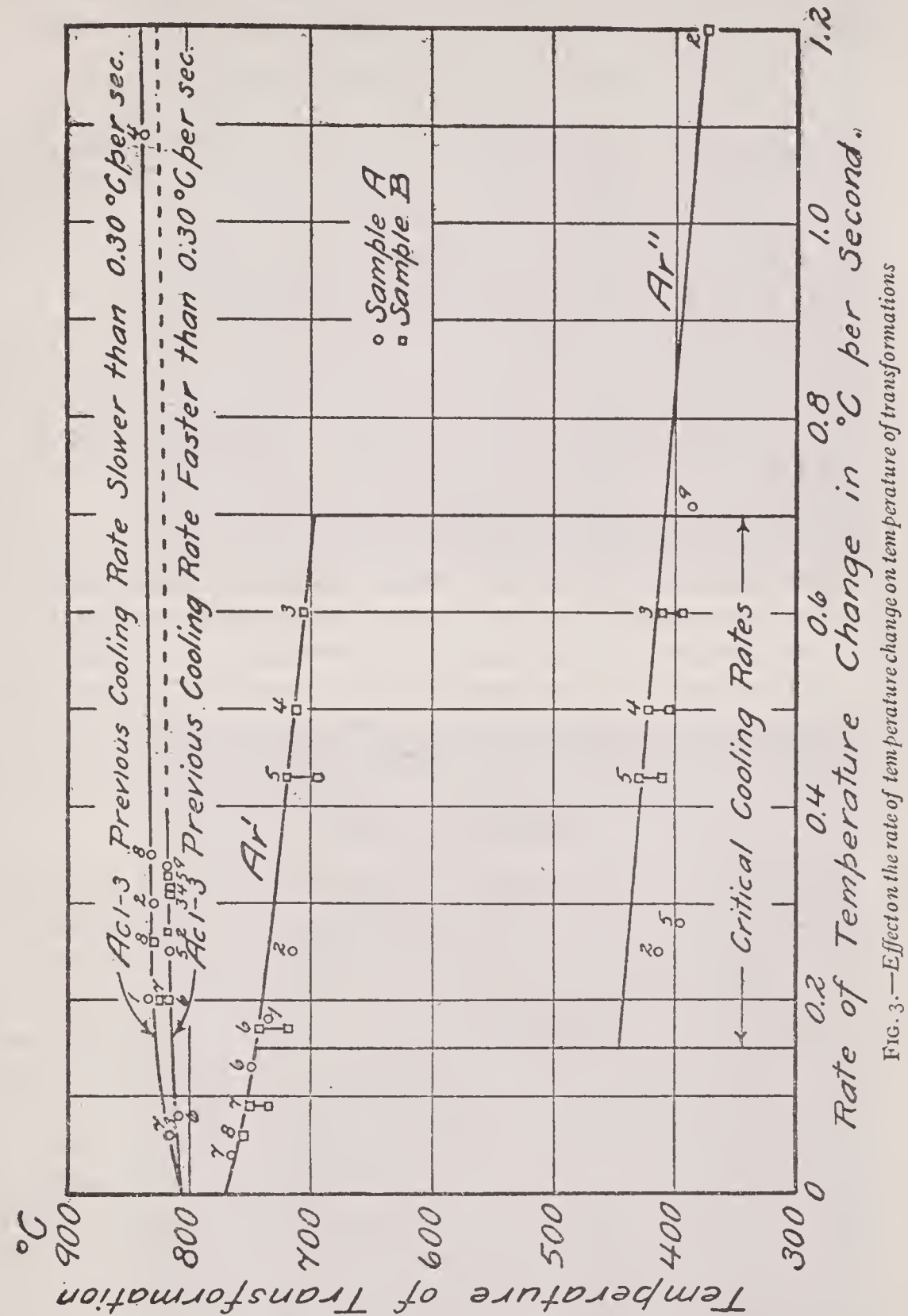


FIG. 3.—Effect on the rate of temperature change on temperature of transformations

Two values for the maximum transformation temperature indicate a double peak. In Fig. 3 the temperature values of $Ac1-3$, Ar' , and Ar'' given in Table I are plotted against rate of temperature

change in degrees centigrade per second. No attempt is made to interpret the double peaks, and the lines representing Ar' and Ar'' in Fig. 3 are rather arbitrarily drawn through the higher values.

V. EFFECT OF COOLING RATE

An inspection of the cooling curves of Figs. 1 and 2 shows that Ar' is the normal Ar_{3-2-1} of slow cooling rates, but that it gradually dies off in intensity with increasing rate. While Ar' is falling off in intensity, the transformation Ar'' comes into existence and gains in intensity, being a maximum for rates that do not show Ar' .

This region over which both Ar' and Ar'' occur, as shown in Fig. 3, will be called the critical cooling range. Its limits were roughly determined as 0.15 and 0.70° C per second, by plotting a measure of the transformation intensities, obtained by a method to be described in a subsequent section, against rate and extending a straight line through the values back to zero.

The remarkable change in properties caused by this very slight change in rate is represented, when the same phenomenon is observed on varying $T_{max.}$, by the considerable temperature variation of approximately 300° C for some high-speed steels.¹⁴

The fact that the split transformation occurs with a constant value of $T_{max.}$ shows that it is unnecessary to hypothecate a dissociation of the carbide (or carbides) to explain this phenomenon.

1. MICROSTRUCTURE¹⁵

To establish the structural difference between the material cooled at a rate that gave Ar' and one that gave Ar'' and the analogy to the phenomena obtained by varying $T_{max.}$ for this steel, micrographs were taken of samples cooled at several definite rates of cooling. The micrograph, Fig. 4, taken after cooling at a rate of 0.01° C per second, Ar' only occurring, shows an irregular mass of fine carbide particles, corresponding to pearlite in carbon steels and distinct from the coarse particles of free carbide, in a ferrite matrix. Figs. 5 and 6, micrographs, taken of samples cooled at rates of 0.30 and 0.33° C per second, respectively, show characteristic black troostite patches on a background of martensite. With those cooling rates the transformations Ar' and Ar'' were both obtained. Fig. 7, which is of sample A following a cooling rate of 0.71° C per second, shows a martensitic structure although the

¹⁴ Honda and Murakami, loc. cit.; Carpenter, loc. cit.

¹⁵ Micrographs by H. S. Rawdon.

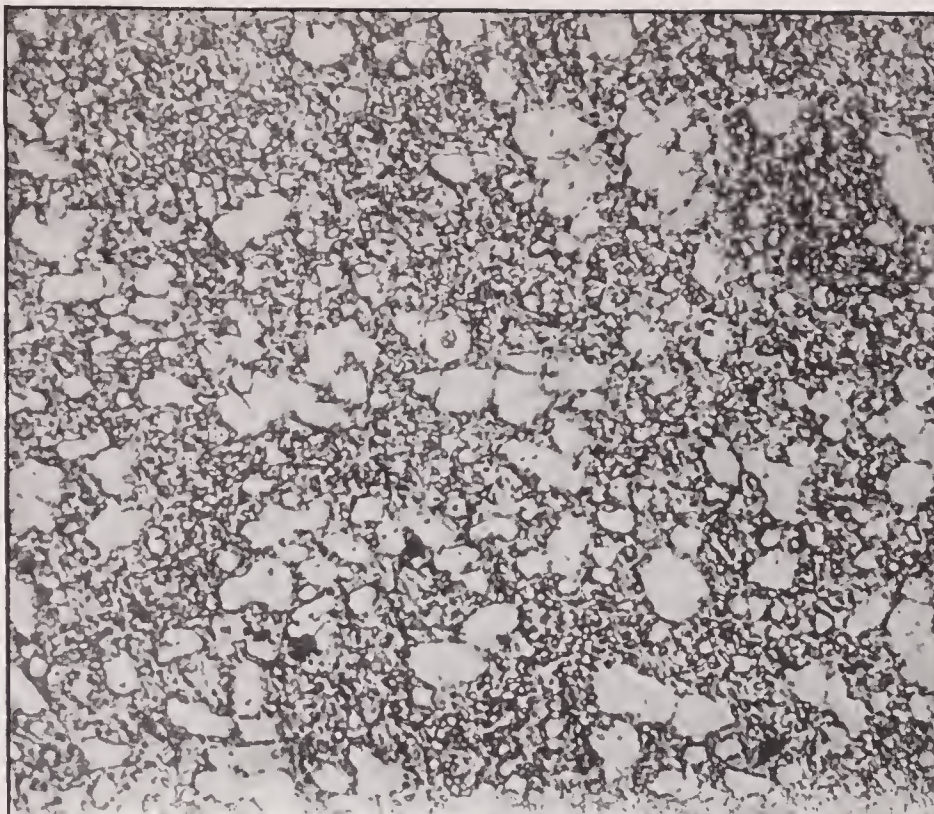


FIG. 4.—Cooling rate, 0.01° C per second. Transformation Ar'
Magnification 1000x. Etched in 2 per cent HNO_3 in alcohol



FIG. 5.—Cooling rate, 0.30° C per second. Transformation Ar' and Ar''
Magnification 1000x. Etched in 2 per cent HNO_3 in alcohol

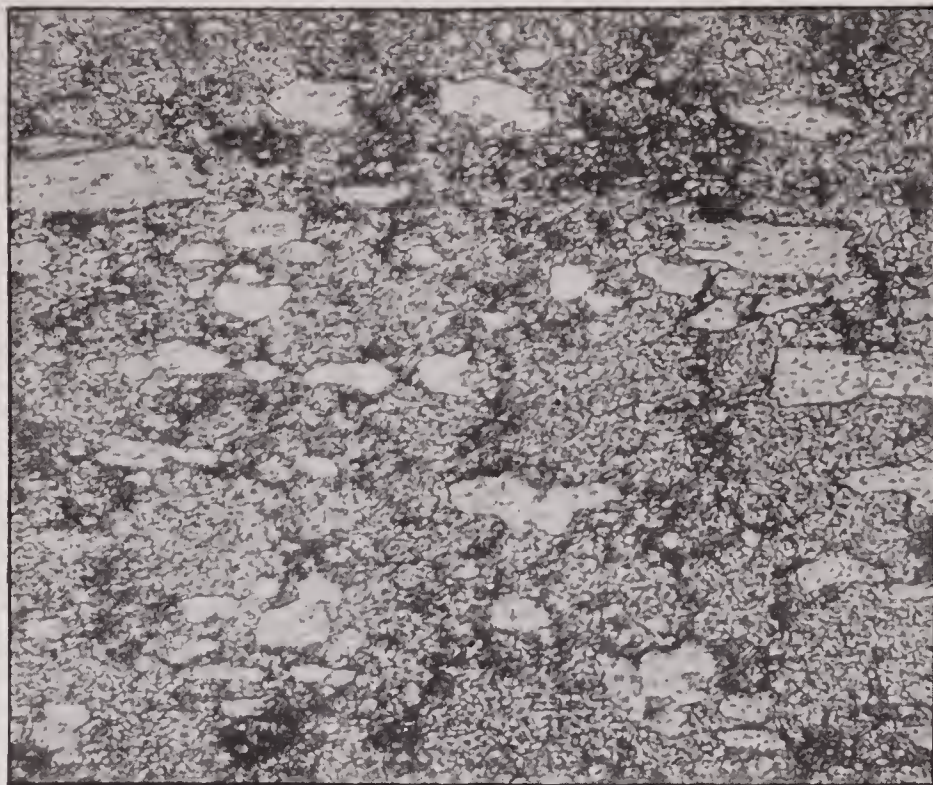


FIG. 6.—Cooling rate, 0.33°C per second. Transformation Ar' and Ar''
Magnification 1000x. Etched in 2 per cent HNO_3 in alcohol

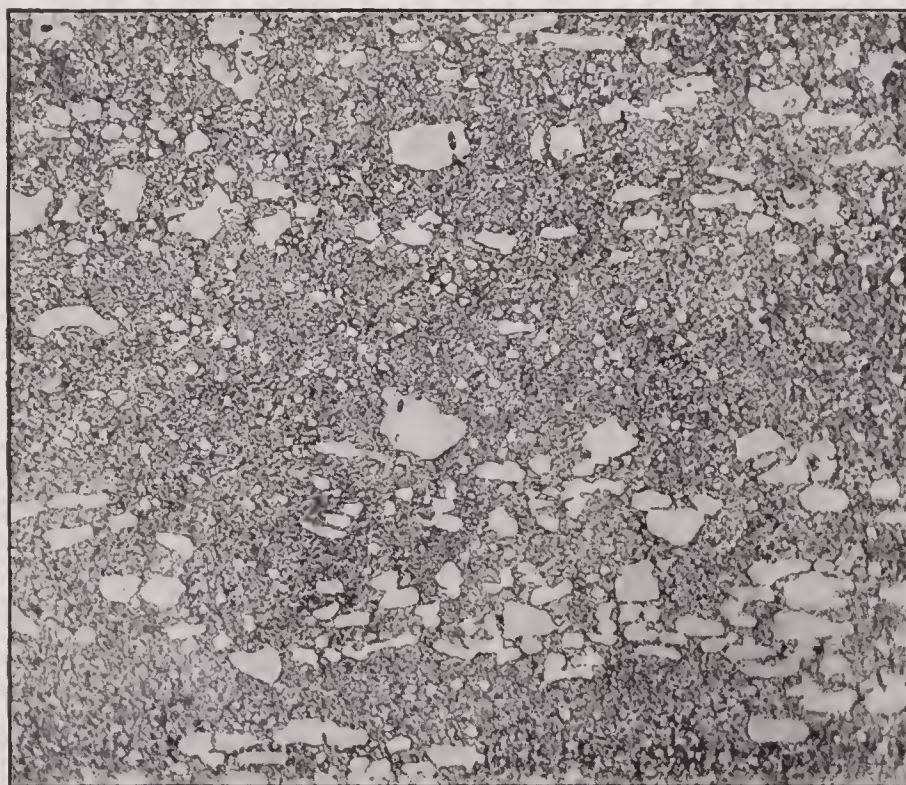


FIG. 7.—Cooling rate, 0.71°C per second. Transformation Ar' and Ar''
Magnification 1000x. Etched in 2 per cent HNO_3 in alcohol

needlelike markings, characteristic of high-carbon steels, are only slightly evident.

The conclusions to be drawn from the preceding microscopic evidence are that troostite or a decomposition product forms with the transformation Ar' and martensite with the transformation Ar'' , precisely what obtains when the same transformations are observed in other alloy steels with varying T_{max} .

2. RELATION OF " Ar' " TO " Ar'' "

The radical structural difference between the material showing Ar' and that showing Ar'' presumes a similar radical difference in the transformations Ar' and Ar'' . To demonstrate the possibility of this difference, the intensities of the transformations $Ac1-3$, $Ac2$, Ar' , and Ar'' have been estimated by means of a planimeter measuring the area of the positive departure of the thermal curves from the assumed neutral body curves through the respective transformation ranges. The results given in Table 2 show a well-marked loss in intensity of the sum of the areas of Ar' and Ar'' at the cooling rate $1.20^{\circ}C$ per second, which gives Ar'' above. On the assumption that Ar'' is no new transformation other than Ar_3 , 2 , or 1 , the conclusion is that some one or more of the transformations Ar_3 , 2 , and 1 constituting Ar' is suppressed.

TABLE 2.—Areas of Thermal Curves in Square Millimeters Corresponding to Heat Effects of Transformations in Sample B

Run	Ac1-3	Ac2	Ac1-3+ transformation Ac2	Cooling rate, de- grees per second	Ar'	Ar''	Ar' trans- forma- tion+Ar''
First.....				3.40			
Second.....	36	74	110	1.20		84	84
Third.....	40	66	106	.60	26	72	98
Fourth.....	40	68	108	.50	38	60	98
Fifth.....	64	64	128	.43	56	48	104
Sixth.....	60	64	124	.17	100		100
Seventh.....	72	72	144	.09	120		120
Eighth.....	72			.06	116		116
Average.....		68	120				

3. SUPPRESSION OF " Ar_1 "

The preceding conclusion agrees with the generally accepted conception that martensite is a solid solution of cementite in some form of iron. This means that Ar_1 is suppressed with the formation of martensite and further evidence is not wanting. The transformation intensities indicate that a heat effect of the mag-

nitude of Ar_1 is missing at Ar'' . The work of Honda on the magnetic properties of tungsten steels in a paper before the September meeting of the Journal of the Iron and Steel Institute, however, shows that the carbide is retained in solution at Ar'' for the carbide in solution does not undergo the transformation A_0 . The transformations Act and Ac_1-3 offer still further substantiation to which attention will be called in their discussion.

There still remains the possibility that one of the other transformations, Ar_3 or 2 , is suppressed. This, however, is manifestly impossible, for A_3 and A_2 coincide when A_3 is depressed below the normal temperature of A_2 ¹⁶ and martensite is magnetic. The magnetic curves of Honda and Murakami¹⁷, taken on a number of tungsten steels showing a split transformation with increasing T_{max} , also indicate the occurrence of A_2 at Ar'' .

The conclusion that must therefore be adopted is that Ar_1 is suppressed with the formation of martensite, or that Ar'' constitutes the transformations Ar_3 and 2 .

VI. TRANSFORMATIONS ON HEATING

The thermal curves of Figs. 1 and 2 show two transformations Ac_1-3 and Ac_2 occurring uniformly within narrow temperature limits and a transformation Act occurring only following certain cooling rates. The identity of Ac_2 is established by its markedly characteristic shape and its uniform occurrence at about 780°C which is in close proximity to its maximum, 768° , in pure iron. This phenomenon of Ac_1 occurring above Ac_2 in alloy steels is not new and has been well established by Moore¹⁸ for a chromium steel. The transformation Ac_1-3 hardly needs identification, although attention should be called to its sluggish ending which indicates that the transformations concerned do not completely coincide. This is further illustrated by the change in area of the peak, which is evidently Ac_1 from the effect of previous cooling rate on its position, with the temperature of its occurrence.

1. TRANSFORMATION " Act "

The transformation Act is indicated by an inflection to the left which denotes an evolution of heat on the heating curve and occurs over a considerable temperature range. It is a maximum following cooling rates that give Ar'' alone, and loses in intensity following decreasing rates through the critical cooling range, becom-

¹⁶ Honda and Takagi, *Sci. Rep. Tohoku Imp. Univ.*, **6**, p. 324; 1918.

¹⁷ Honda and Murakami, *loc. cit.*

¹⁸ Moore, *J. Iron and Steel Inst.*, **81**, p. 268; 1910.

ing zero when Ar' alone occurs. It is therefore roughly proportional in intensity to Ar'' or the amount of martensite present. By its analogy to tempering the conclusion may be drawn that Act represents the precipitation of the carbide in solution to form at first troostite and as it progresses the coarsening of the carbide.

This phenomenon of a heat evolution on heating steels that show Ar'' was observed by Carpenter¹⁹ on differential thermal curves with which T_{max} was varied and connected with tempering.

The nature of Act , a gradual building up of the heat evolution over a long temperature range, may throw some light on the spontaneous heat evolution and also the change in other physical properties of quenched steels as observed by Hadfield and Brush²⁰, by Matsushita²¹, and by Campbell²². The indications are that the transformation starts to a minute degree at very low temperatures, possibly at ordinary temperatures, particularly in carbon-steels which temper at lower temperatures than alloy steels.

The existence of Act as an evolution of heat following cooling rates that give Ar'' is further confirmation of the suppression of Ar_I with the formation of martensite.

2. EFFECT OF PREVIOUS COOLING RATE ON " $Act-3$ "

It will be seen on examining Fig. 3 that practically all the temperature values for the maximum of $Act-3$ lie on two smooth curves. The data of Table 1 show that the runs which correspond to the numbers on the upper curve were obtained following cooling rates that gave Ar' predominant and those on the lower curve following cooling rates that gave Ar'' predominant. The temperature interval, 10° to 15° C, between those two curves may therefore be attributed to the state of division of the carbide resulting from the previous heat treatment.

The phenomenon noted in the preceding paragraph offers still further substantiation of the suppression of Ar' with the formation of martensite.

It may be of interest to note that the curves of Fig. 3 drawn through the temperature values of $Act-3$ and Ar' do not point toward a common equilibrium temperature Ae_I .

¹⁹ Carpenter, J. Iron and Steel Inst., **67**, p. 433; 1905.

²⁰ Hadfield and Brush, Proc. Royal Soc., **93**, p. 188; 1917.

²¹ Matsushita, Sci. Rep. Tohoku Imp. Univ., **7**, p. 43; 1918.

²² Campbell, Reprint J. Iron and Steel Inst., **98**, p. 421; 1918.

VII. SUMMARY

The results of previous investigators have been taken to show that with the occurrence of a split transformation on cooling alloy steels from increasingly higher temperatures (a) that when the higher temperature transformation Ar' is observed with low values of T_{max} , troostite or a decomposition product results and (b) that when the lower temperature transformation Ar'' is observed with high values of T_{max} , martensite is the resulting product.

The present investigation has shown for a certain alloy steel that on varying the rate of cooling, the maximum temperature remaining constant, a strictly analogous phenomenon is observed, increasing rate of cooling having the same effect as increasing T_{max} .

Conclusions are drawn to the effect that—

(a) The transformation Ar' consists of the transformations Ar_3 , 2, and 1.

(b) The transformation Ar'' consists of the transformations Ar_3 and 2.

(c) The transformation Ar_1 , suppressed when Ar'' is observed, occurs on heating as Act with an evolution of heat and the formation of troostite or a coarser condition of the carbide.

(d) The maximum of the transformation $Act-3$ occurs at a higher temperature when the previous cooling rate gave Ar' than when it gave Ar'' .

The author desires to express his indebtedness to H. S. Rawdon for the micrographic work and to Miss P. L. Thompson for her skillful assistance in preparing the experimental data.

WASHINGTON, December 23, 1918.



